

IConUSAS Meeting July 9-10, 2003

The UNICAT Ultra-Small-Angle X-ray Double-Crystal Diffractometer at the Advanced Photon Source

A.J. Allen^a, J. Ilavsky^{a,b}, P.R. Jemian^c and G.G. Long^a

^aNIST, Gaithersburg, MD 20899

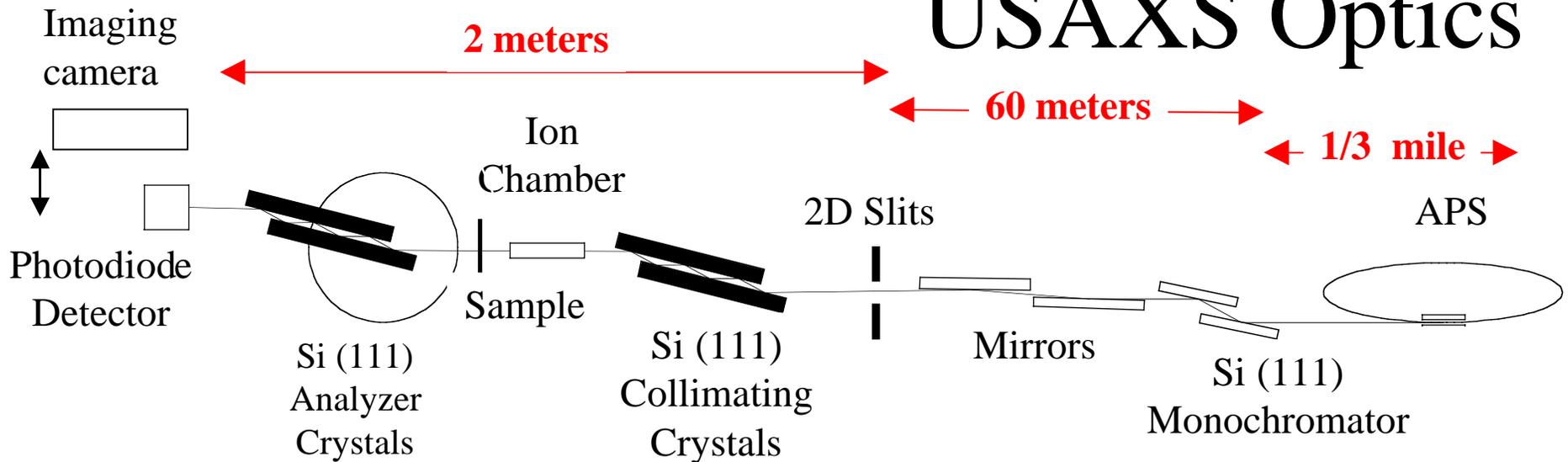
^bPurdue University, West Lafayette, IN 47907

^cUniversity of Illinois, Urbana, IL 61801

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

UNICAT

USAXS Optics



Bonse-Hart USAXS Optics at 33ID

- **Si (111) Monochromator – X-ray Beam Energy Selection**
 - **Mirrors – Harmonic rejection**
 - **2D Slits – Beam Size Definition**
- **Collimating Crystals – Vertical Beam Collimation**
 - **Ion Chamber – Intensity Monitor**
- **10^{13} ph s⁻¹ at 10 keV, 7 keV - 19 keV x-ray energy range**
- **Independent Analyzer Crystals – Rotate to scan scattered x-rays**
- **Photodiode Detector – Linear Dynamic Range of 10+ Decades**
- **Primary standardless, attenuatorless intensity calibration**

NIST

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

USAXS at a 2nd generation synchrotron x-ray source (X23A3, NSLS, Brookhaven):

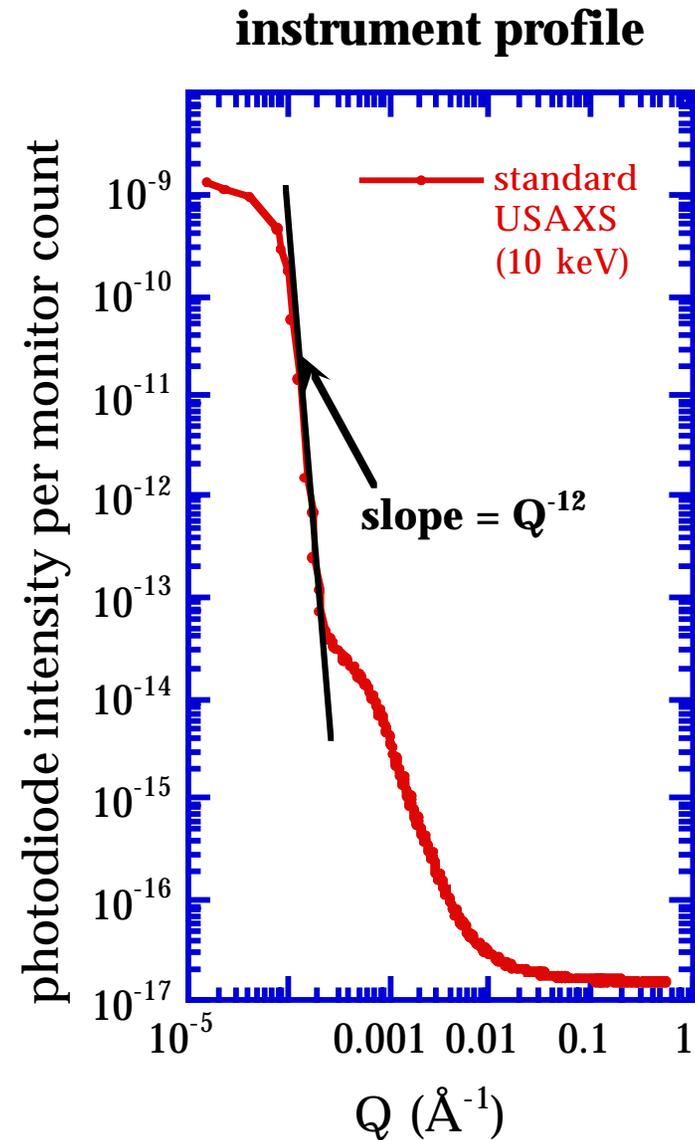
- *bridges the gap between light scattering and conventional pinhole SAXS cameras;*
- *small ΔQ resolution (4×10^{-4});*
- *fluorescence rejection, inelastic scattering rejection;*
- *10-decade intensity range on detector;*
- *primary absolute calibration with no beamstop, so high sensitivity at low Q;*
- *high energy resolution enabling anomalous SAXS capabilities;*
- *very high signal-to-noise ratio for Bonse-Hart due to surface interaction at crystals;*
- *sample radiography using x-ray video camera;*
- *slit-smear desmearing capability;*
- *compact design.*

USAXS at a 3rd generation synchrotron x-ray source (UNICAT, sector 33, APS, Argonne):

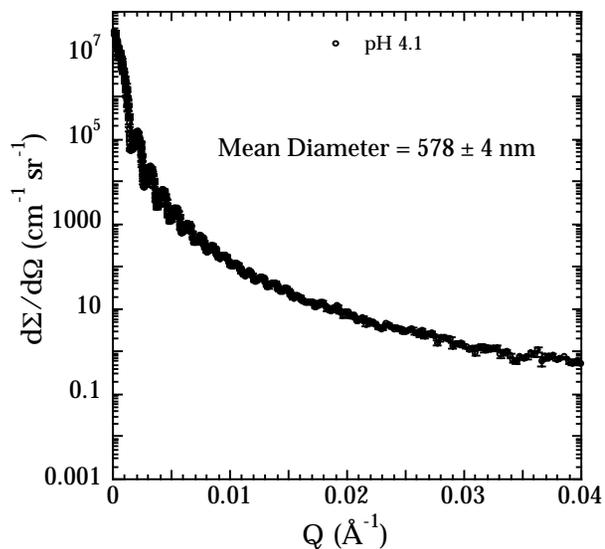
- *slit to pinhole extension of Q-range;*
- *choice of 2, 4, 6 or 8 reflections on each monolith giving option for much greater sensitivity at low Q;*
- *variable geometry and slit-length;*
- *small and highly flexible beam size: 20 μm - 0.6 mm H x 0.1 mm - 2.0 mm W;*
- *improved sensitivity giving over 9-decade intensity range from peak to background;*
- *Q-range 0.0001 \AA^{-1} - 1.0 \AA^{-1} with Si(111) optics;*
- *sample environments for tensile stage, heater, liquid cell, sample changer;*
- *on-line experimental control, data reduction, and preliminary analysis;*
- *option for side-bounce reflection stage configuration to remove slit-smearing effects with anisotropic scatterers (SB-USAXS).*

STANDARD USAXS:

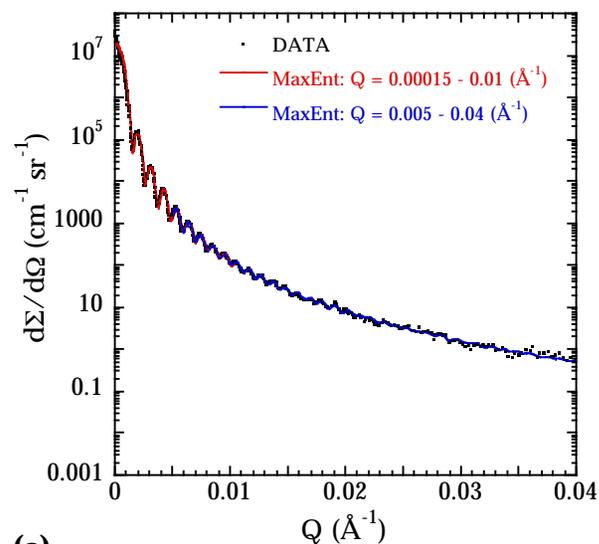
Ultrasmall-angle x-ray scattering (USAXS) utilizes Bonse-Hart double-crystal optics to extend the Q-range of SAXS down to ultralow Q values. However, in the standard configuration, data are inherently slit-smeared.



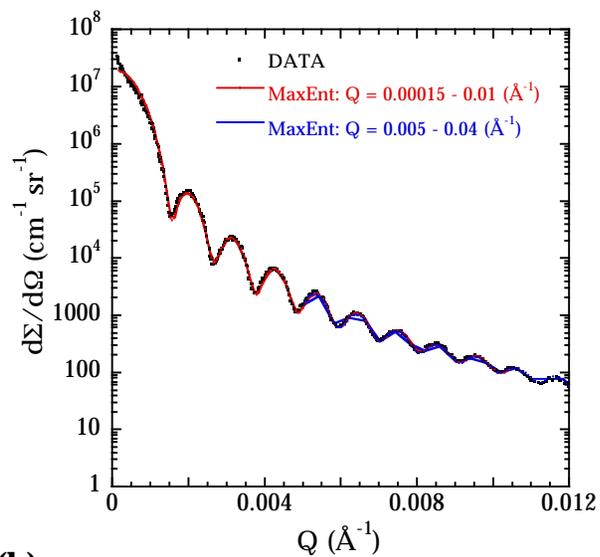
Silica pH 4.1 Desmeared USAXS Data



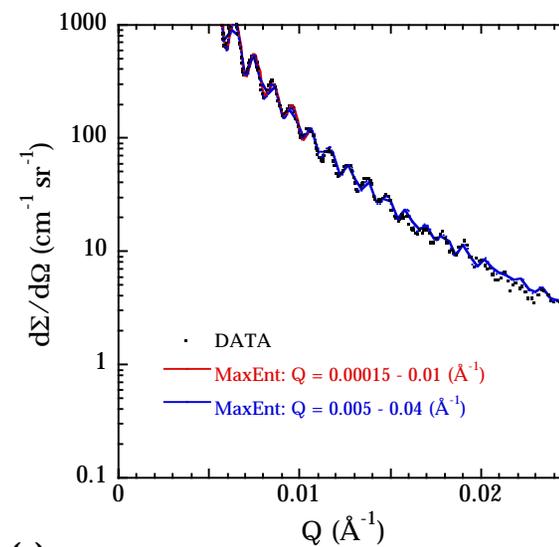
Silica pH 4.1 Fits



(a)

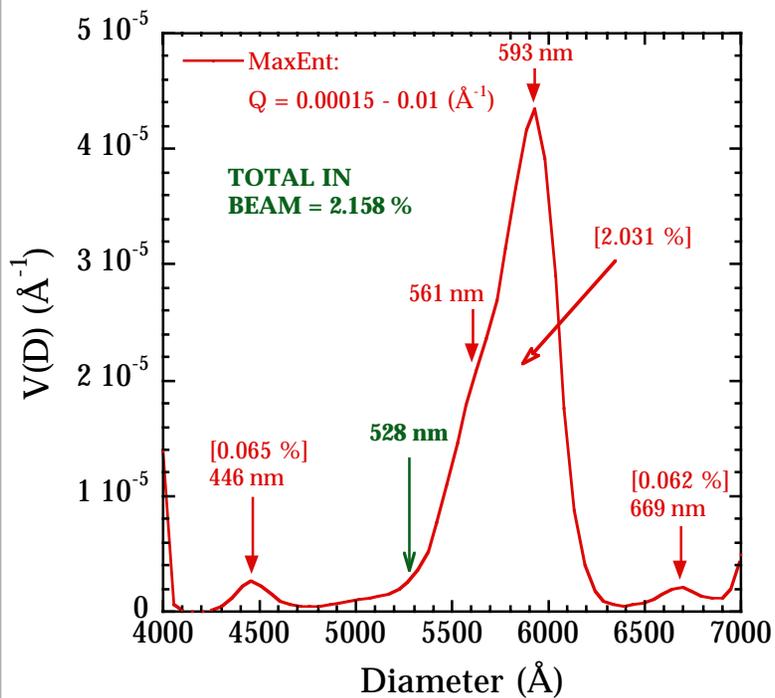


(b)

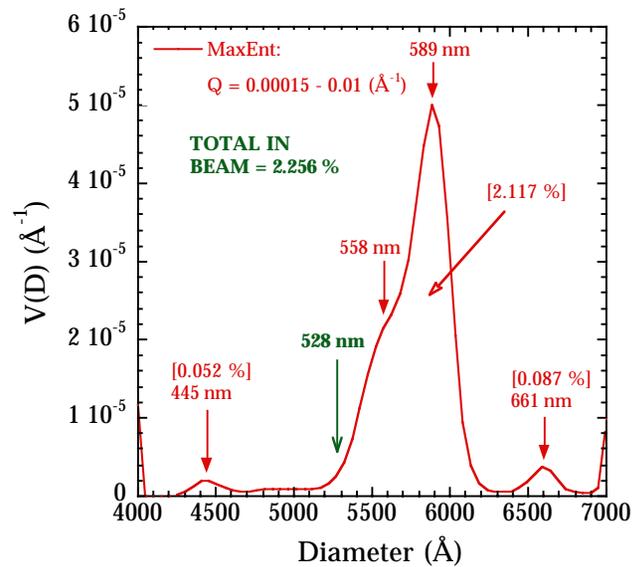


(c)

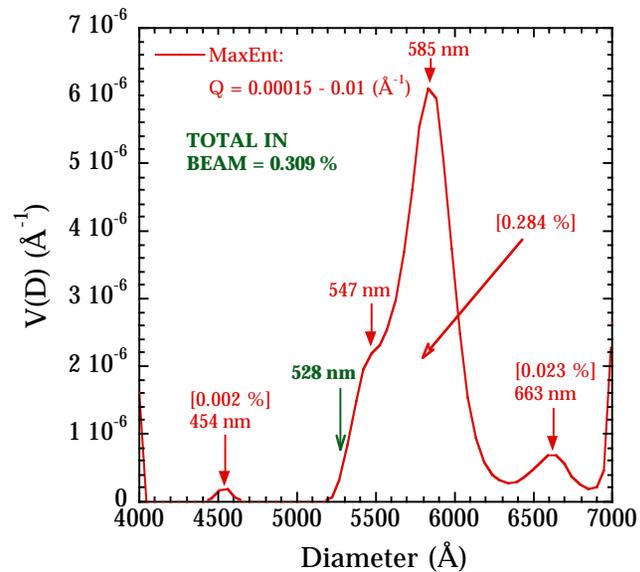
Silica pH 7 MaxEnt Volume Size Distribution



Silica pH 4.1 MaxEnt Volume Size Distribution

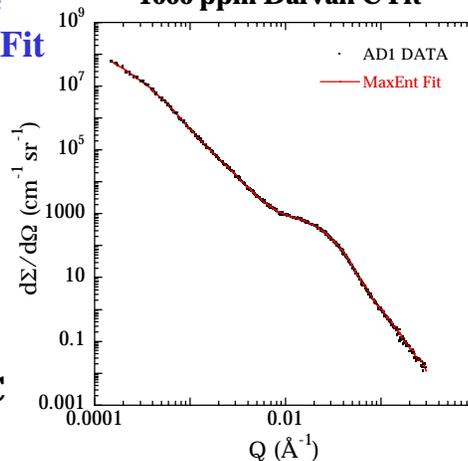


Silica pH 9 MaxEnt Volume Size Distribution

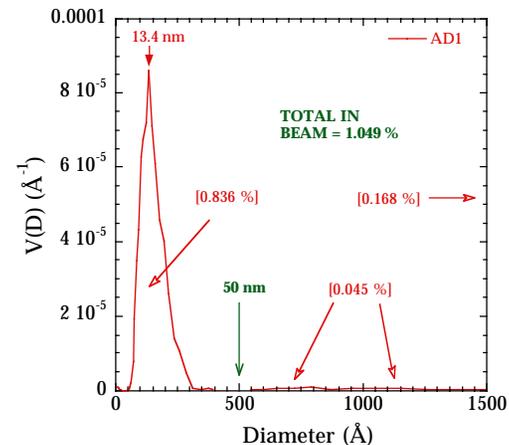


MaxEnt Size Distribution Fit

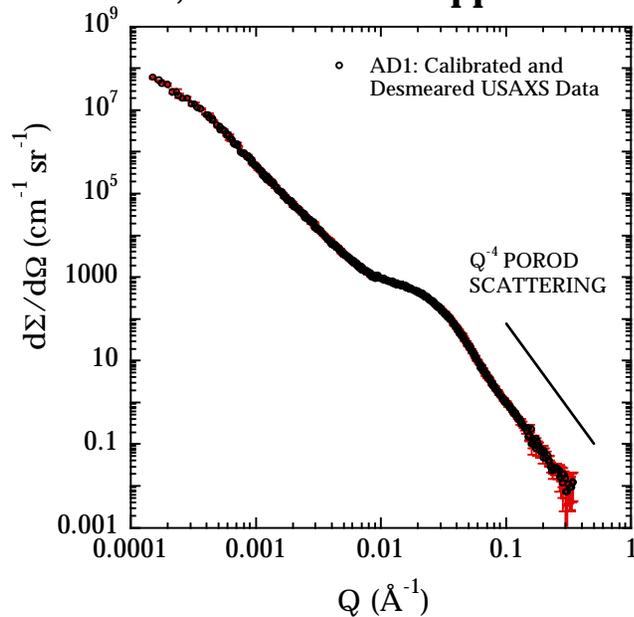
Alumina, 2 % vol. in 1000 ppm Darvan C Fit



Alumina 2 % vol. in Darvan C: MaxEnt Volume Size Distribution



Alumina, 2 % vol. in 1000 ppm Darvan C



Fractal Model Fit

Primary particle diameter = 13.69 nm ± 0.23 nm

Fine-particle volume fraction = 1.42 % ± 0.08 %

Coarse-particle volume fraction = 0.66 % ± 0.03 %

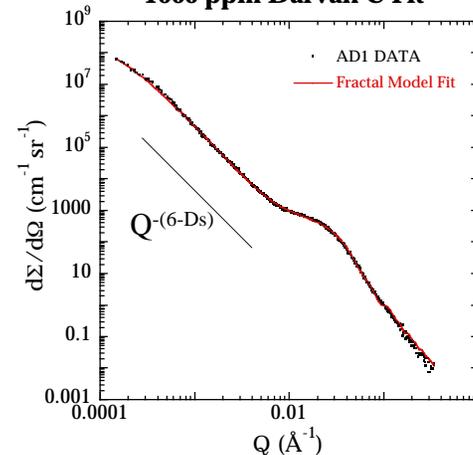
Surface-fractal D_s = 2.838 ± 0.015

Correlation length (upper-limit) for surface-fractal scaling = 781 nm ± 24 nm

Surface in surface-fractal = (0.750 ± 0.102) m² cm⁻³

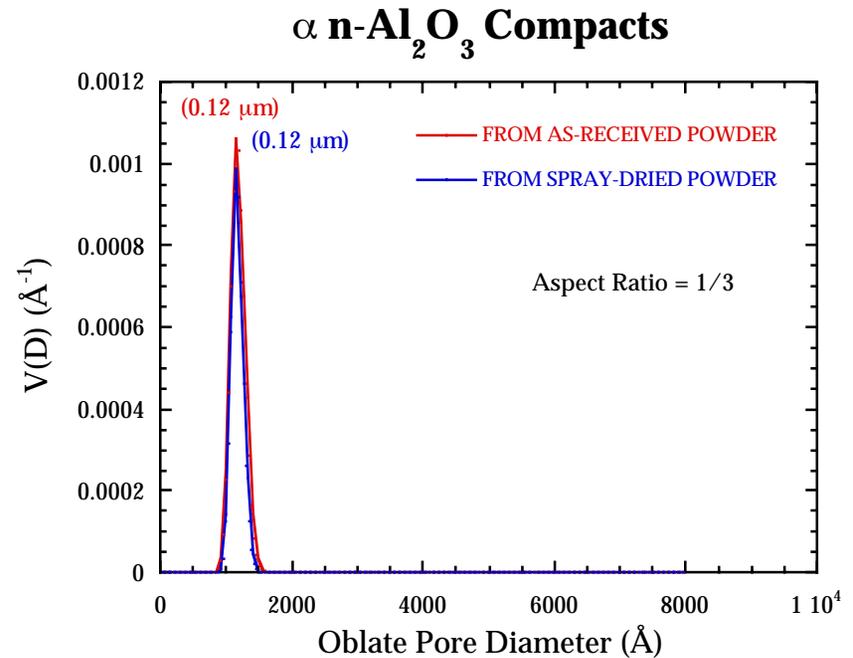
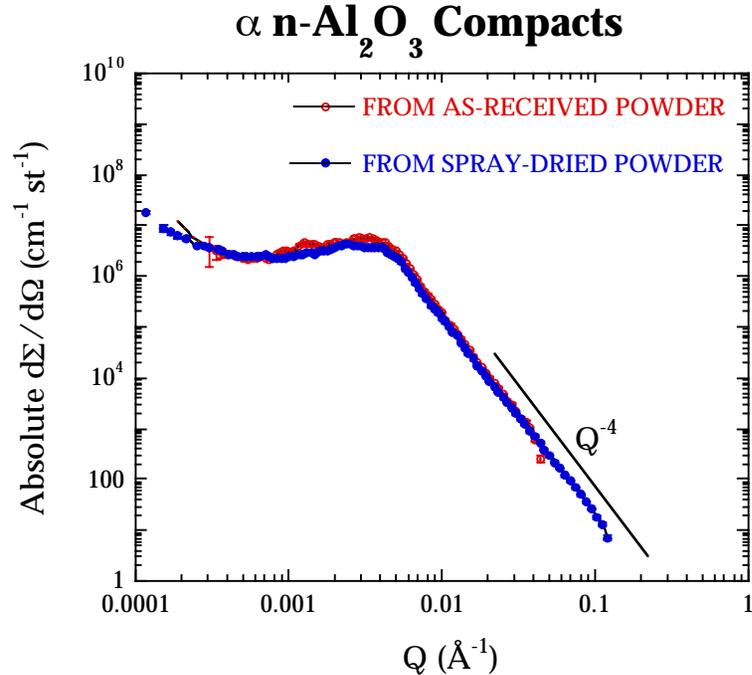
Non-fractal surface = (2.94 ± 0.47) m² cm⁻³

Alumina, 2 % vol. in 1000 ppm Darvan C Fit

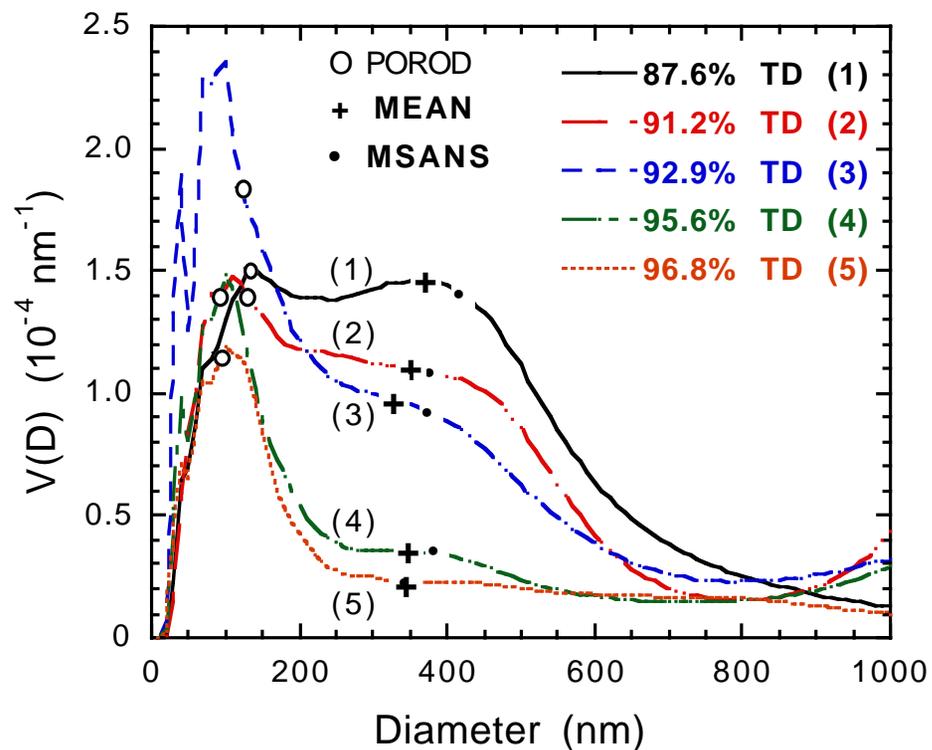


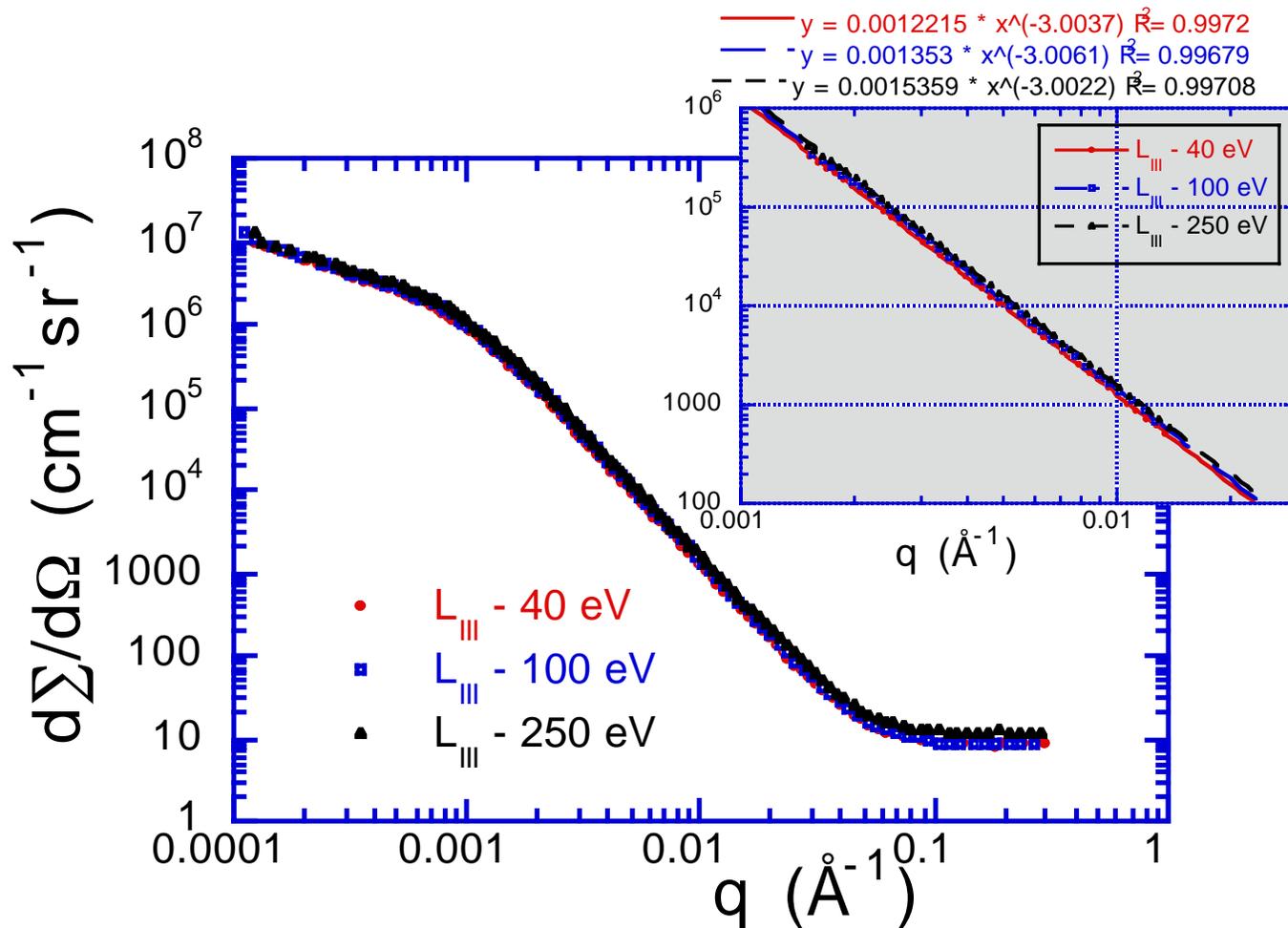
Measured Porod surface area = (3.935 ± 0.30) m² cm⁻³

Use of Modified Percus Yevick Methods to Analyze Size Distribution in the Presence of Interparticle Interference Scattering Effects



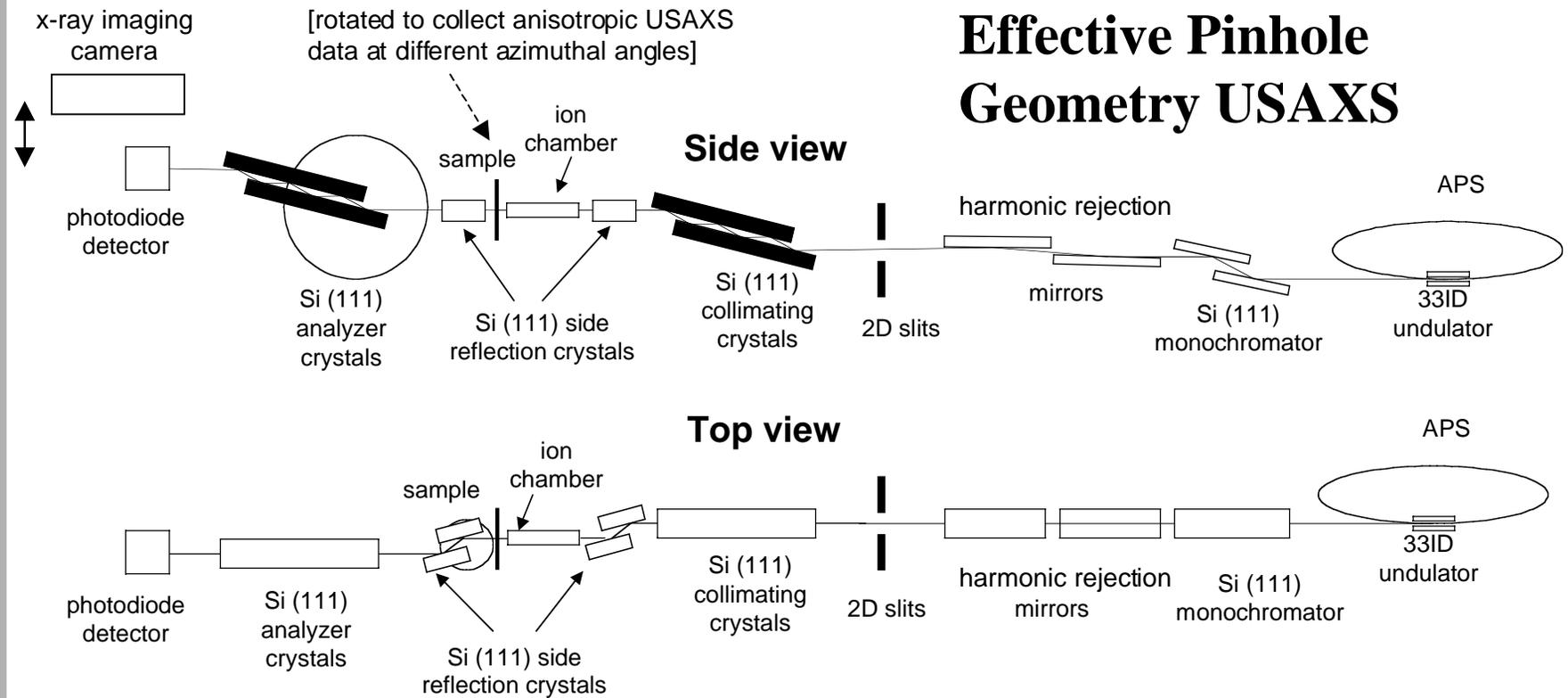
Si_3N_4 : Comparison of MSANS, Porod (SANS) pore diameters with mean pore diameters derived from MaxEnt pore size analysis of USAXS data:





ASAXS results for Si_3N_4 containing rare-earth precipitates

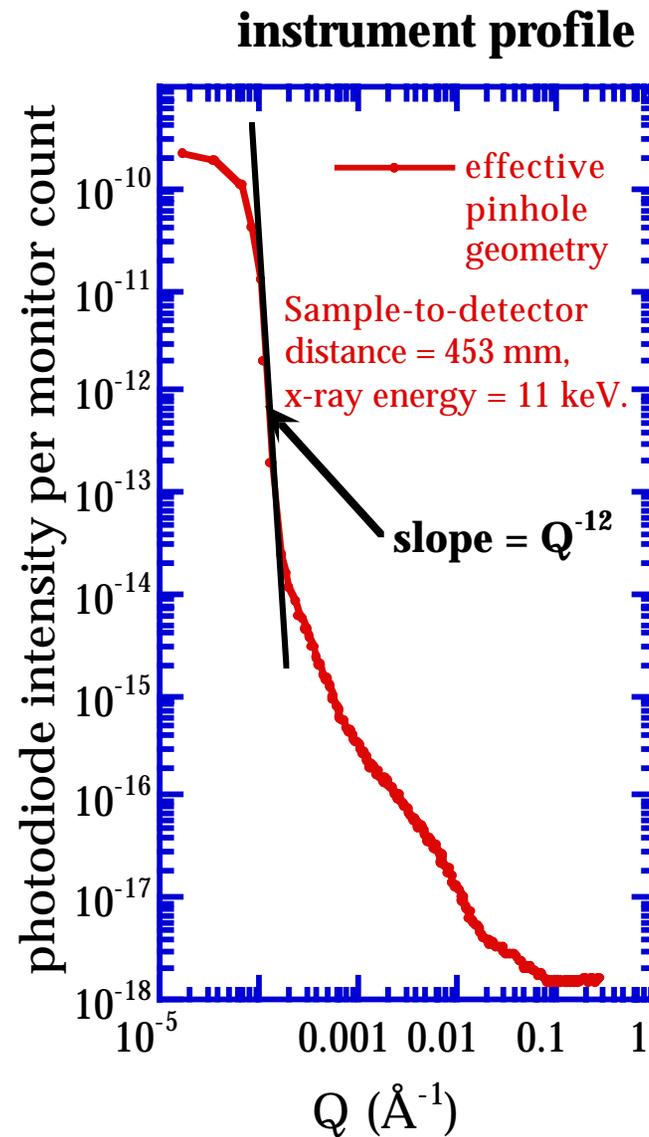
Anisotropic Ultrasmall-Angle X-ray Scattering (USAXS) Studies - at APS UNICAT 33-ID



SB-USAXS:

With the use of side-bounce reflection stages to remove the slit-smearing effect, an effective pinhole collimation is achieved.

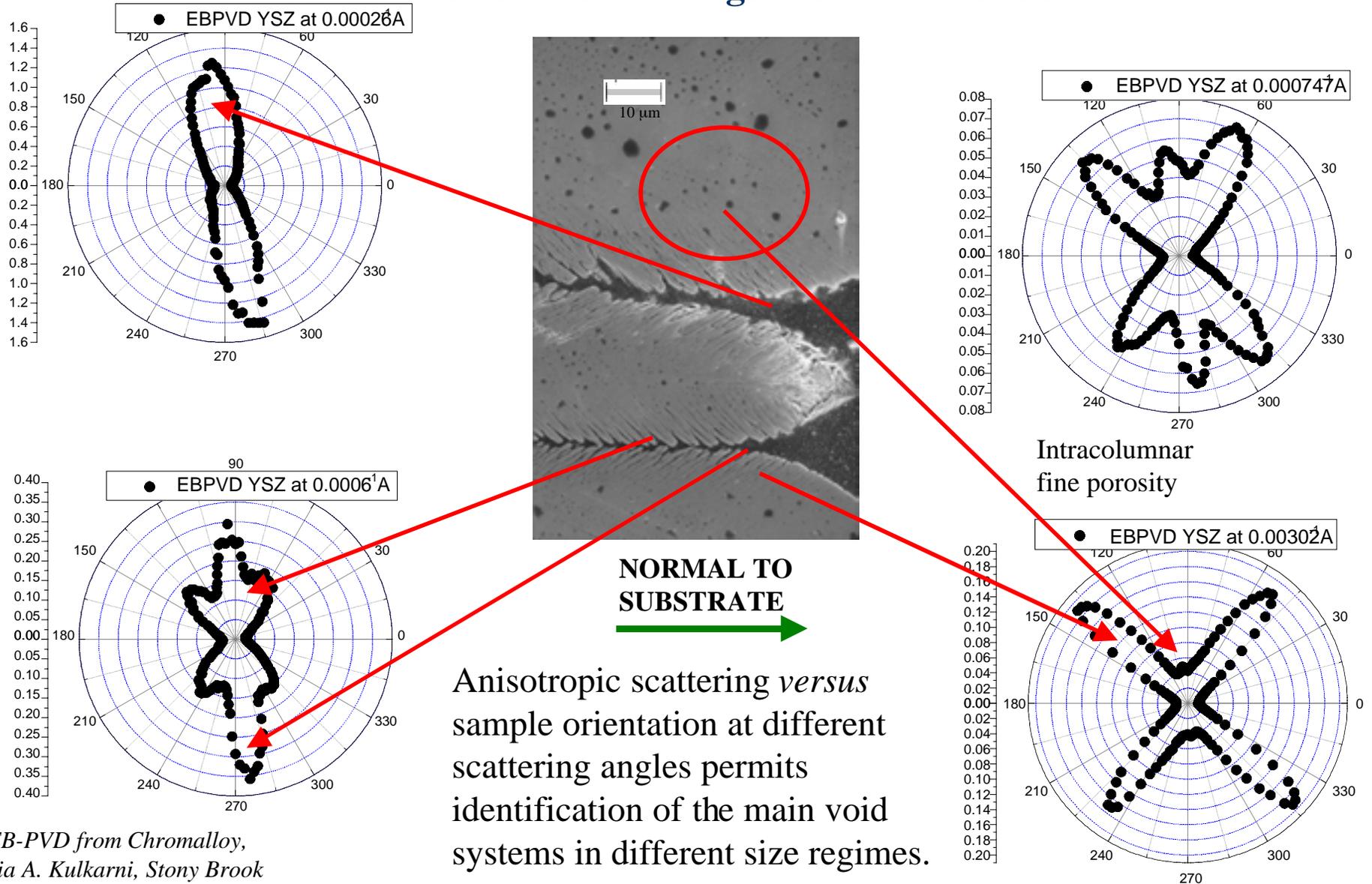
Pinhole or side-bounce USAXS (SBUSAXS) is suitable for the characterization of anisotropic microstructures.



Anisotropic Ultrasmall-Angle X-ray Scattering (USAXS)

– microstructure characterization of 400 μm - 500 μm thick

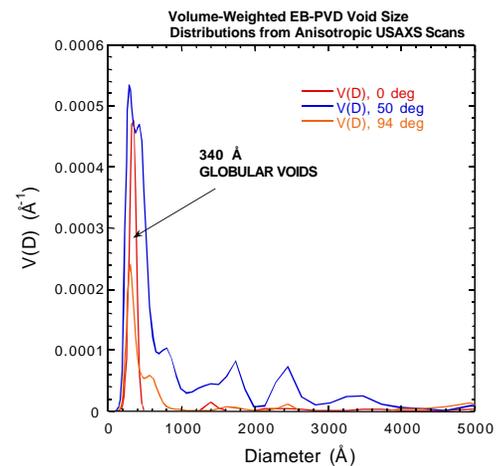
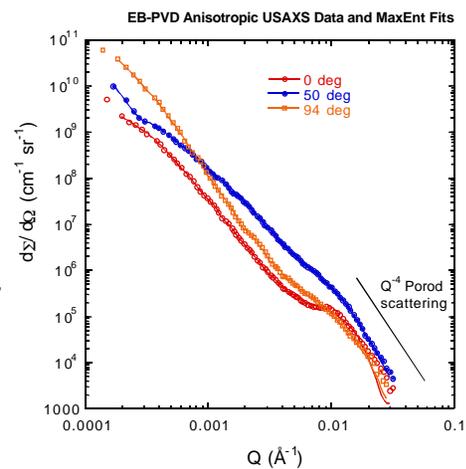
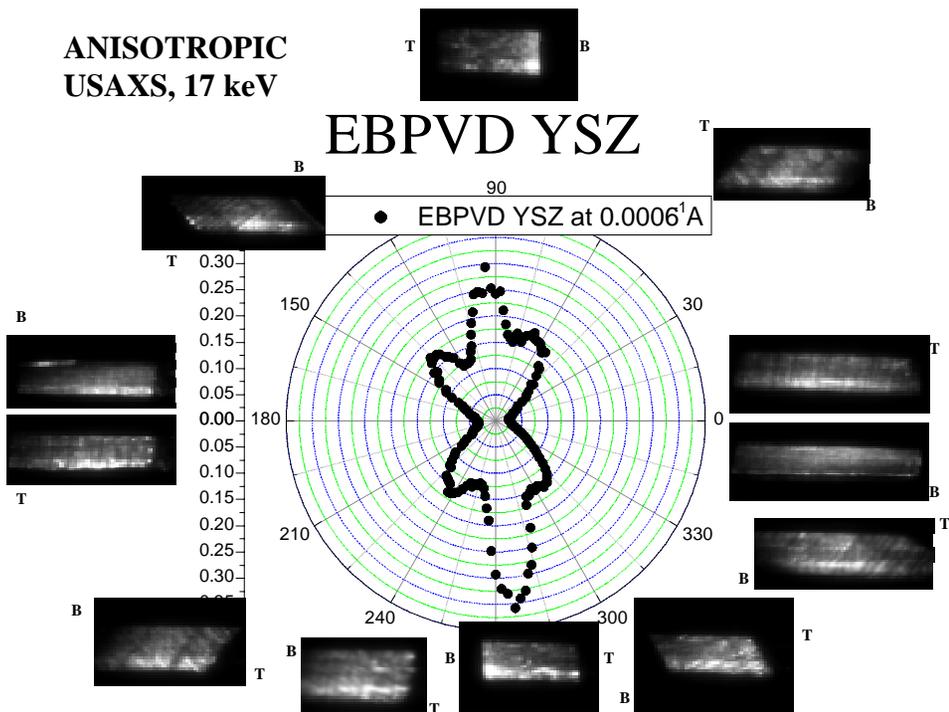
EB-PVD thermal barrier coatings *in situ* on the substrate.



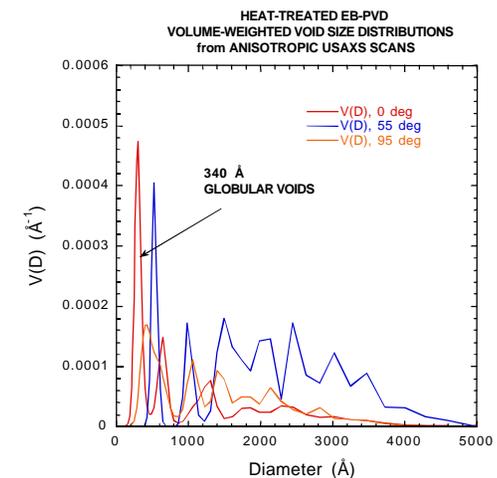
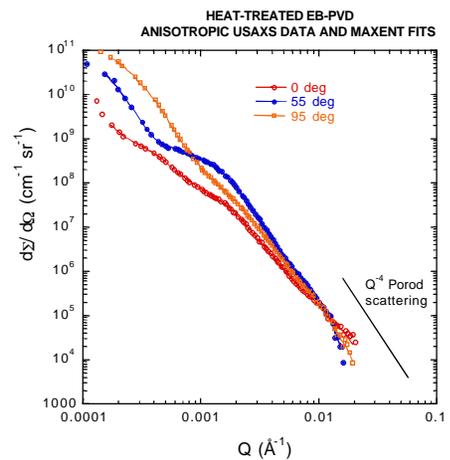
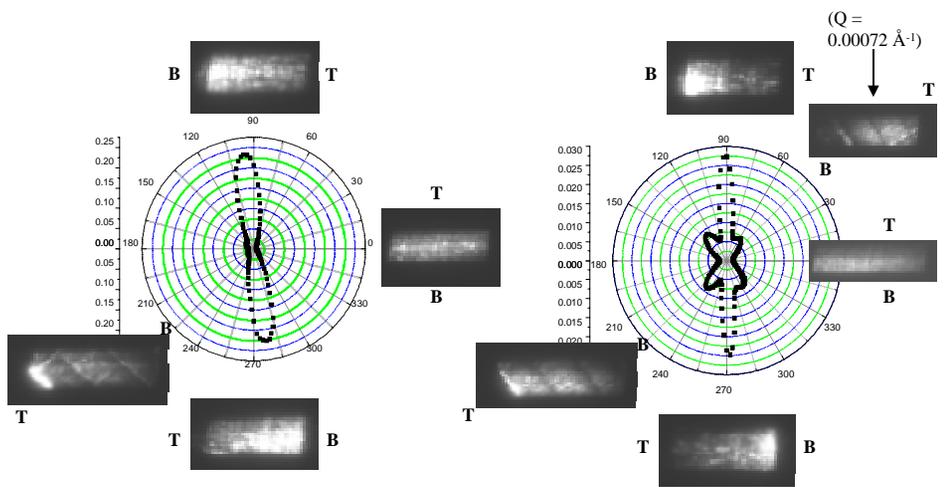
EB-PVD from Chromalloy,
via A. Kulkarni, Stony Brook

**ANISOTROPIC
USAXS, 17 keV**

EBPVD YSZ



**EB-PVD Thermally Cycled
{(1150°C/30mins + 30 mins cooling) x 10}**



4-COMPONENT VOID ANISOTROPIC USAXS MODEL:

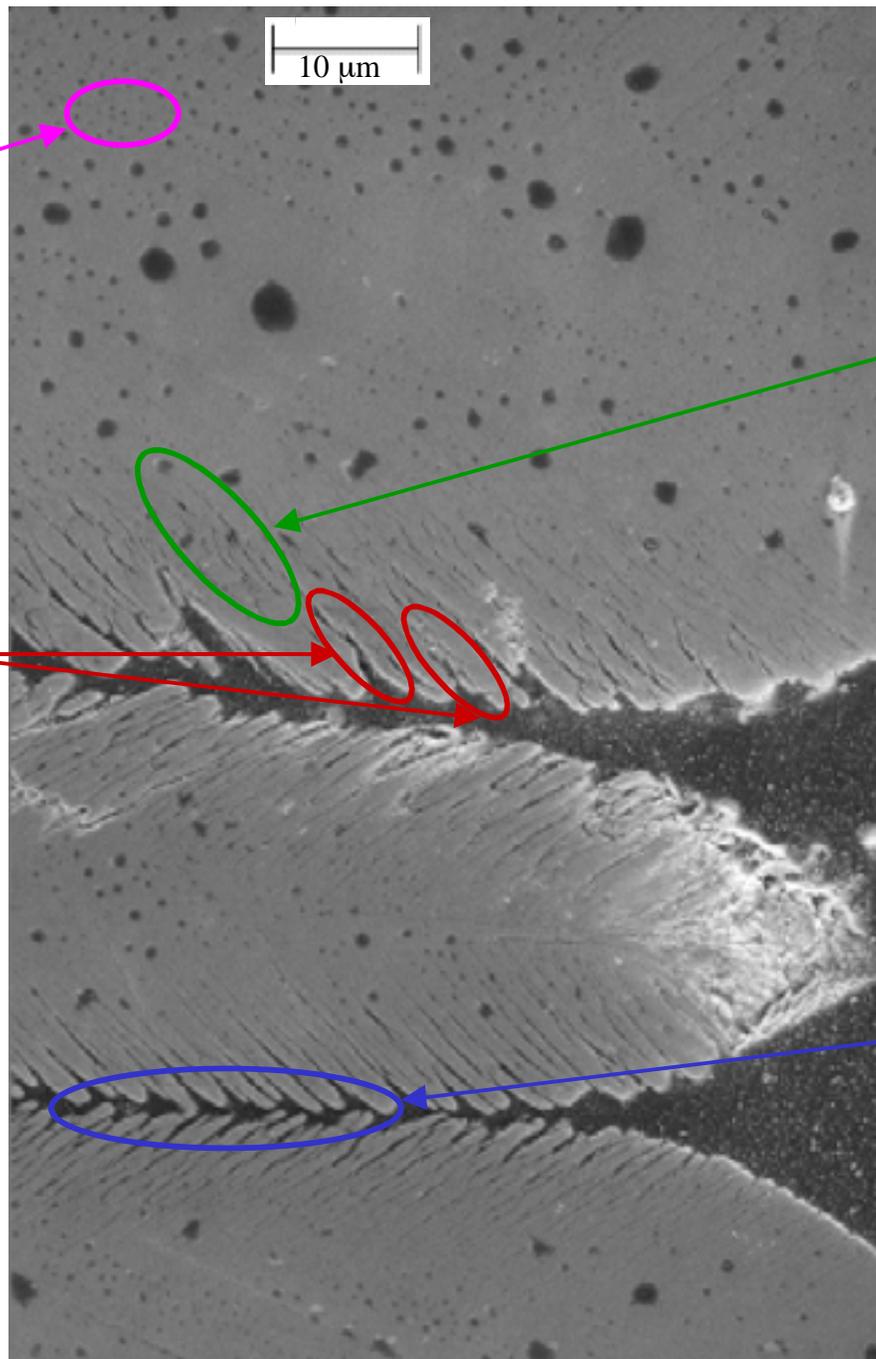
Measure anisotropic USAXS data in all 3 (X, Y, Z) sample orientations with sufficient azimuthal resolution to capture anisotropy and model each of 4 component void populations with non-random distributions of spheroids:

$$\left. \frac{d\sigma_i}{d\Omega} \right|_{\Omega, Q} = \int_0^{\pi/2} d\alpha \int_0^{2\pi} d\omega \left\{ P_i(\alpha, \omega) \frac{d\sigma_i(Q, X_i)}{d\Omega} \sin \alpha \right\}$$

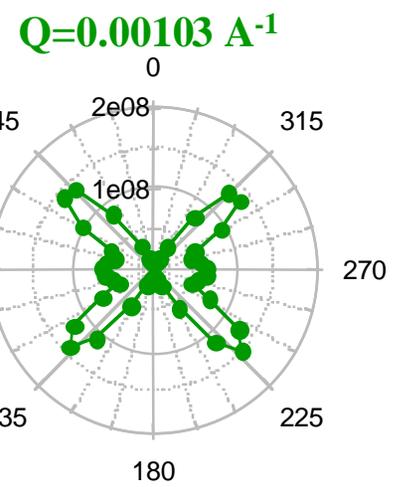
where $i = 1 \dots 4$, $P_i(\alpha, \omega) = A_i(\alpha) \cdot W_i(\omega)$, and:

$$\frac{d\sigma_{\beta, X}}{d\Omega} = V^2 |\Delta\rho|^2 \frac{9\pi}{2} \left\{ \frac{J_{(3/2)}[QR_0 K(\beta, X)]}{[QR_0 K(\beta, X)]^{(3/2)}} \right\}^2 \quad \text{with:}$$

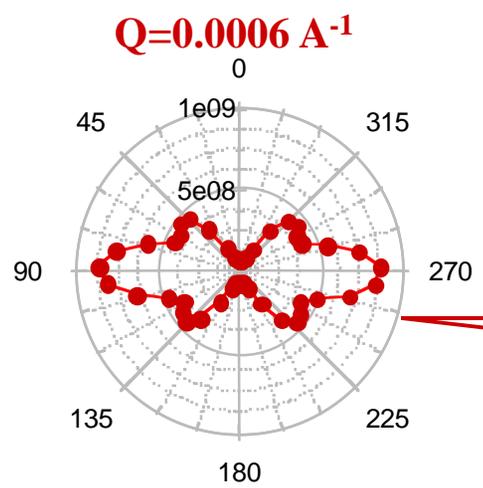
$$A_i(\alpha) = a_3 + |\cos(\alpha - a_1)|^{a_2} \quad \& \quad W_i(\omega) = w_3 + \left| \cos\left(\frac{\omega - w_1}{2}\right) \right|^{w_2}$$



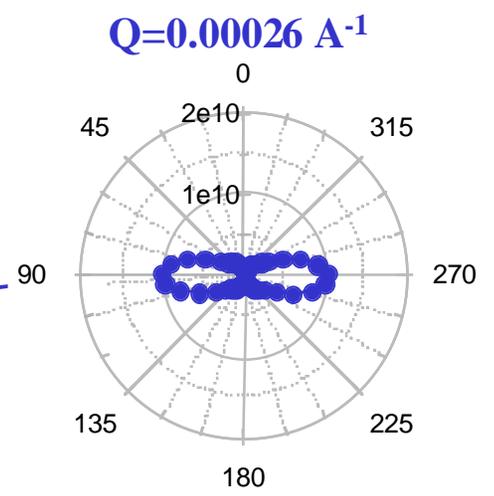
(4) Nanometer Globular Voids



(3) Fine Intracolumnar Voids



(2) Coarse Intracolumnar Voids



(1) Intercolumnar Voids

USAXS 4-component Model:

TOTAL POROSITY: 22.56 %

(1) INTERCOLUMNAR PORES:

POROSITY: $6.12 \pm 0.02 \%$

<O.D.>: $721.9 \pm 1.0 \text{ nm}$

[Aspect Ratio = 0.110, 85° to substrate]

(2) COARSE FEATHER PORES:

POROSITY: $3.93 \pm 0.01 \%$

<O.D.>: $190.6 \pm 0.2 \text{ nm}$

[Aspect Ratio = 0.068, 49° to substrate]

(3) CONNECTED nm-PORES:

POROSITY: $3.84 \pm 0.01 \%$

<O.D.>: $33.2 \pm 0.1 \text{ nm}$

[Aspect Ratio = 0.050, 49° to substrate]

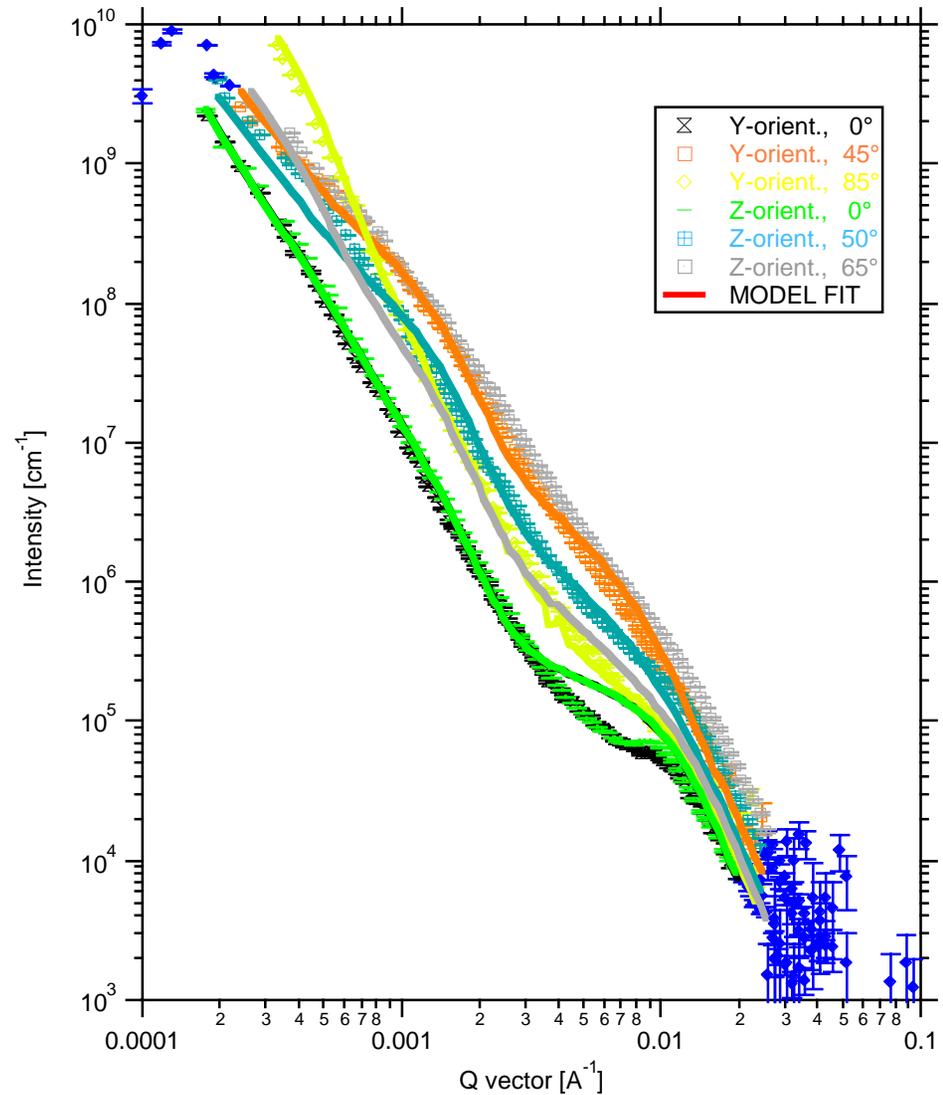
(4) GLOBULAR nm-PORES:

POROSITY: $8.67 \pm 0.04 \%$

DIAMETER: $39.1 \pm 0.8 \text{ nm}$

[MEAN DIMENSIONS =

$39.1 \times 39.1 \times 27.4 \text{ nm}$]



Advantages of 2D-Collimated USAXS

Small beam size and high x-ray brilliance make pinhole USAXS (SBUSAXS) practical for the study of anisotropic materials.

By rotating the sample about the incident beam, anisotropic USAXS data can be obtained where both the maximum length-scale probed and the anisotropic resolution surpass those achievable with conventional pinhole SAXS and a 2D detector.

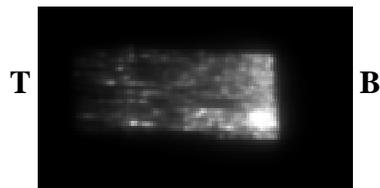
2D-Collimated *versus* Conventional USAXS Trade-off:

There is a trade-off in using the pinhole USAXS configuration in place of the conventional configuration:

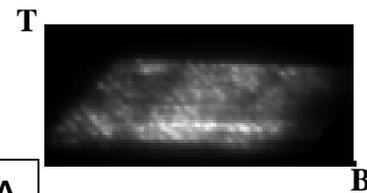
Conventional USAXS data are slit-smearred but can be readily desmeared for isotropic scattering. However, anisotropic scattering cannot be desmeared without full knowledge of the anisotropy in the scattering.

Anisotropic USAXS data are unsmearred, but the additional optical components increase the background, reducing the maximum attainable Q .

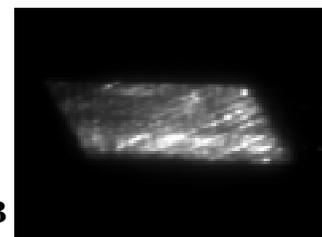
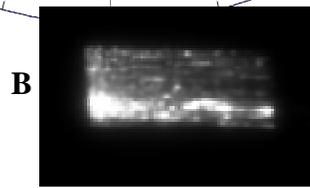
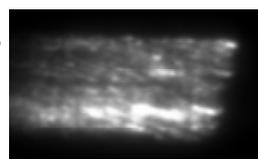
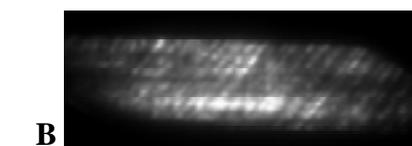
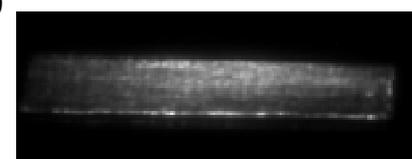
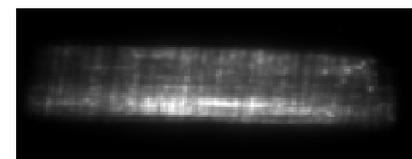
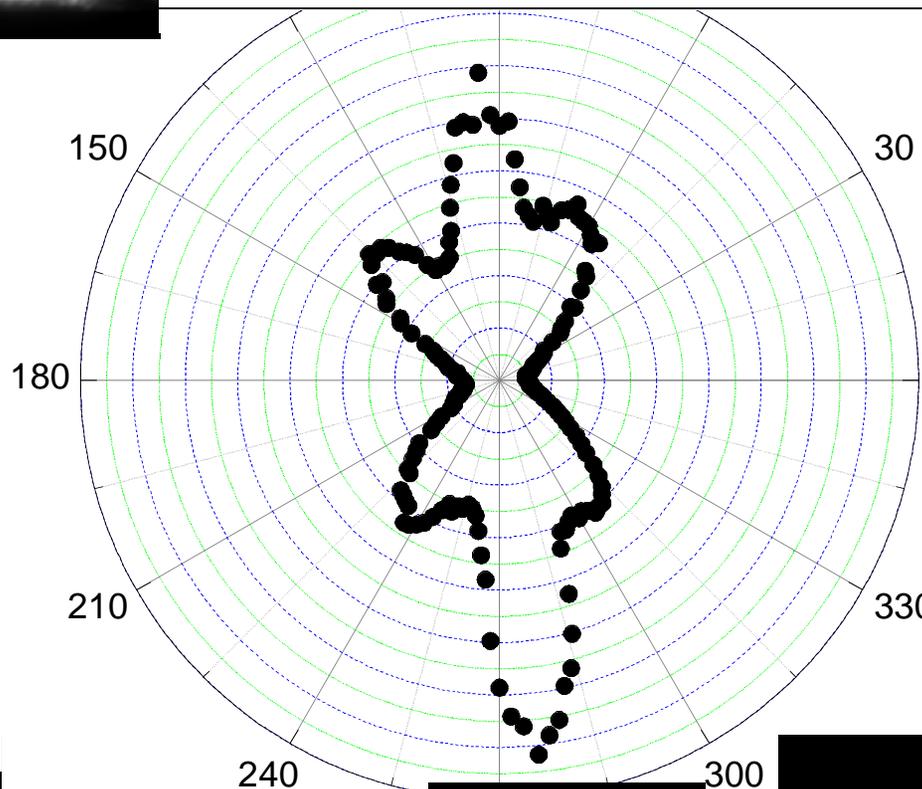
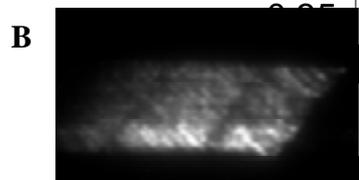
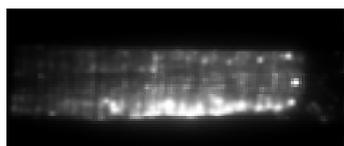
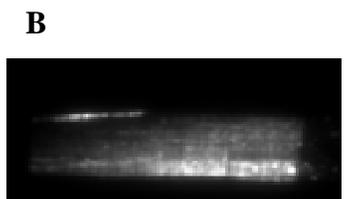
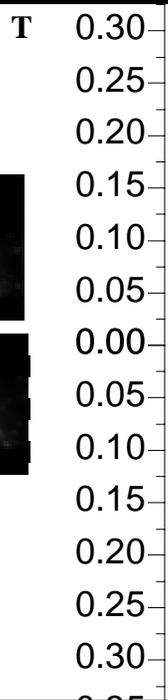
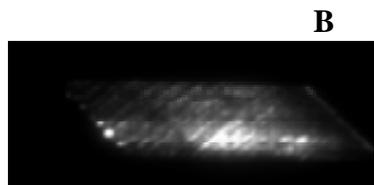
ANISOTROPIC USAXS, 17 keV



EBPVD YSZ



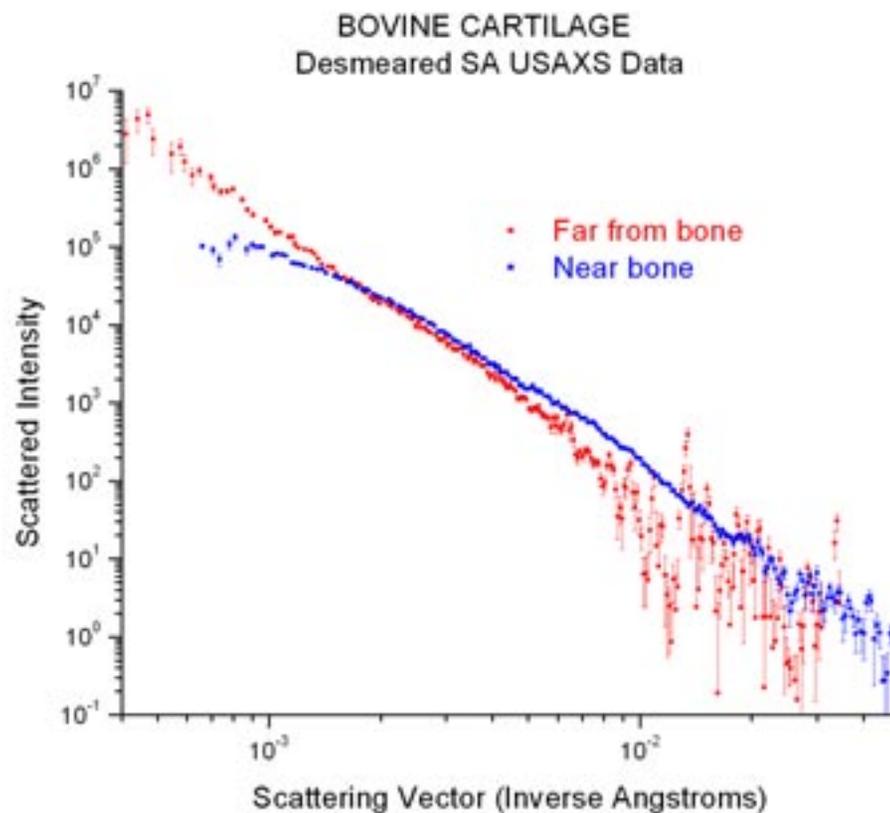
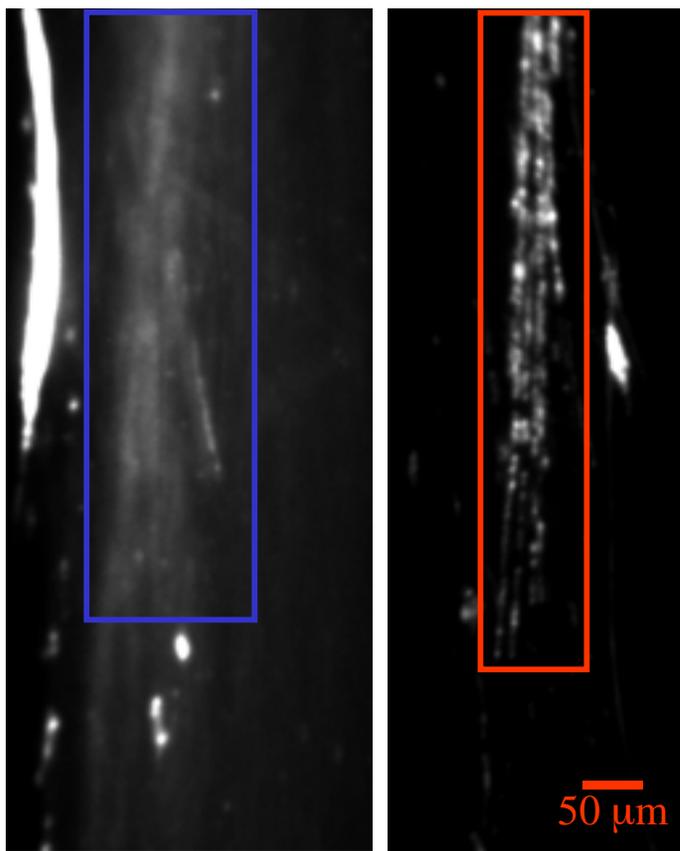
● EBPVD YSZ at 0.0006°



T

B

Bovine Cartilage - Rush Medical College/NIST



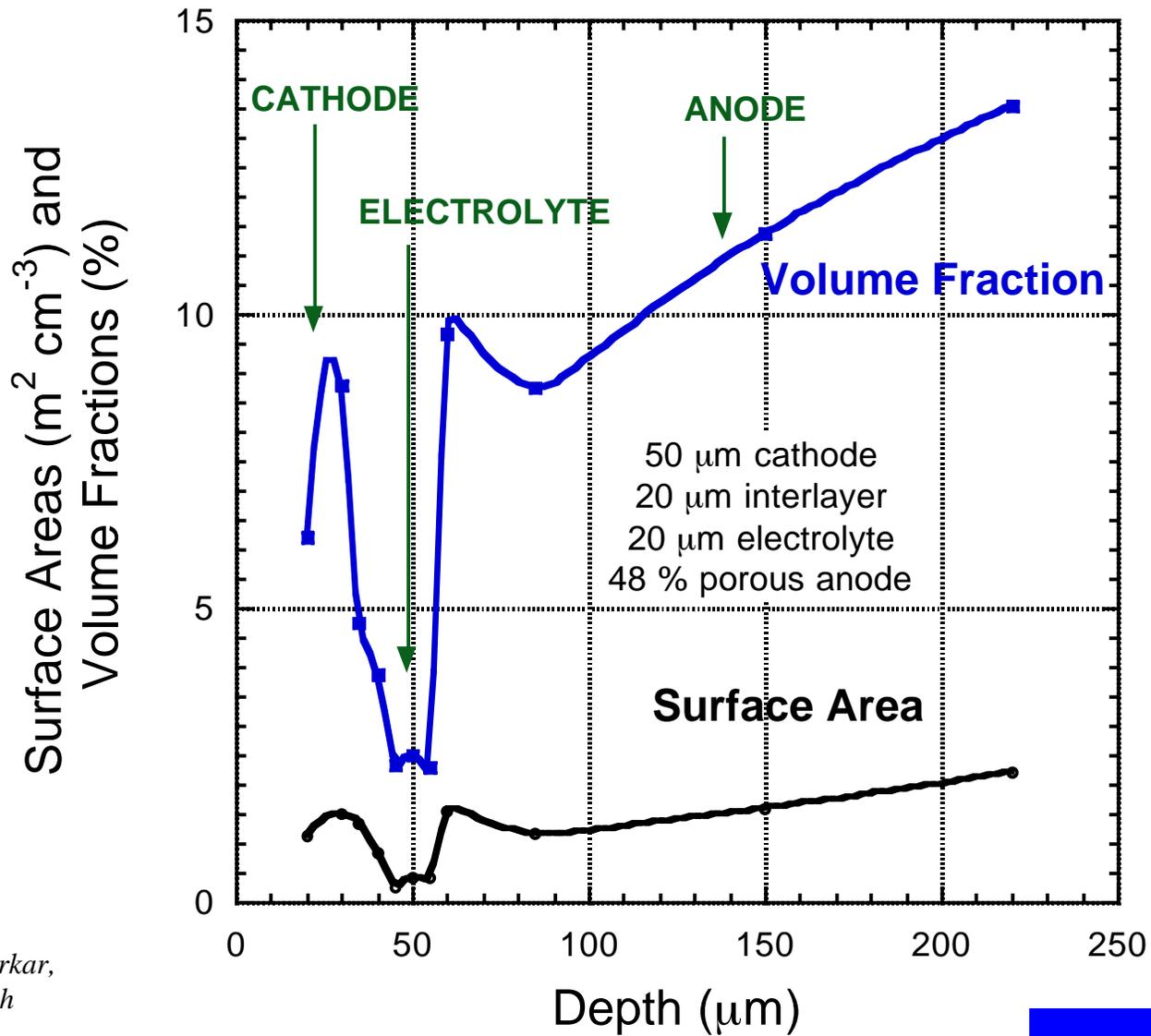
$$q = 0.0005 \text{ \AA}^{-1}$$

$$\text{Resolution} = 1.5 \text{ \mu m}$$

$$E = 17.0 \text{ keV}$$

Sample thickness $\approx 1 \text{ mm}$

SOFC: 20 μm electrolyte layer



SOFC from A. Virkar,
University of Utah

Ceramics Division, Materials Science & Engineering

Examples of Application:

- sintering resistance in advanced thermal coatings
- gradient microstructures in fuel cell layers
- nanoparticle agglomeration and assembly
- hierarchical polymer structures
- nanocomposites and nanotubes
- cement hydration and soil structure
- precipitation in alloys
- polymer deformation
- creep phenomena in Si_3N_4
- dislocation structures in aluminum
- diesel soot formation and in situ nanoparticle formation within flames

CONCLUSIONS:

Both USANS and USAXS have undergone major development in the last decade.

Each technique extends the regular SANS/SAXS Q range to allow studies of features up into the micrometer + size regime.

Major challenge for USANS is in migration to pulsed neutron sources.

Major challenge for USAXS is to combine small beam size and anisotropic configurations at increasingly brilliant x-ray sources, and exploit fully USAXS imaging.

Selected References:

- [1] G.G. Long, P.R. Jemian, J.R. Weertman, D.R. Black, H.E. Burdette and R.D. Spal, *J. Appl. Cryst.*, **24**, 30 (1991).
- [2] A. J. Allen, P. R. Jemian, D. R. Black, H. E. Burdette, R. D. Spal, S. Krueger and G. G. Long, *Nucl. Instr. and Meth. in Phys. Res. A* **347**, 487 (1994).
- [3] G.G. Long, A.J. Allen, J. Ilavsky, P.R. Jemian and P. Zschack, in 'Synchrotron Radiation Instrumentation: Eleventh U.S. National Conference,' Ed.P. Pianetta, J. Arthur and S. Brennan, AIP Melville, NY, 183 (2000).
- [4] J. Ilavsky, A.J. Allen, G.G. Long, P.R. Jemian, "Effective Pin-hole collimated ultra-small angle x-ray scattering instrument for measuring anisotropic microstructures", *Review of Scientific Instruments* **73**[3] 1660 (2002).

Acknowledgments:

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....and, of course, all of our collaborators and users !